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Photoconductivity and Photovoltage Generation in Novel Photocrosslinkable Nonlinear Optical Polymers

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13. ABSTRACT (Maximum 200 Words)

Photoconductivity in photocrosslinkable second order nonlinear optical (NLO) polymeric materials and photovoltage generation in a poled guest-host polymer are reported. These NLO polymers have been functionalized with crosslinkable cinnamoyl groups and show relatively stable second order optical nonlinearities at room temperature when poled and crosslinked. Without introducing any photosensitizer or charge carrier transport agents, photoconductivity was obtained in these polymer systems. Optical excitations of the NLO chromophores lead to photocarrier generation and it is conjectured that these NLO chromophores also play a role in the carrier transport. In addition to photoconductivity, photovoltage generation was observed in the dye doped polymer upon poling. This poled polymer also exhibits a polarization dependent photovoltage when illuminated by light in the absorption region of the NLO chromophore.

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photocrosslinkable nonlinear optical polymer, photovoltage generation, guest-host

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polymer. These polymeric materials can also be readily processed into good optical quality thin films. Such polymeric photorefractive media may be particularly attractive for waveguide applications.

To exhibit the photorefractive effect, a material must show photoconductivity and the linear electro-optic effect. Schildkraut [5] observed photoconductivity in a photoconducting electro-optic polymer, in which photoconductivity was achieved by the addition of perylene photosensitizer and triarylamine hole transport molecules to an NLO polymer where the NLO moiety—stilbene was incorporated in the polymer host. The calculated photorefractive figure of merit was 2.45 pm/V for this polymeric material. Ducharme *et al.* [6] and Moerner *et al.* [7] reported on the photorefractive effect in two NLO polymers—bisA-NPDA and NNDN-NAN. Photocurrent generation in these polymers originated from the NLO chromophores—NPDA and NAN. However, charge transport was realized by adding one of the following hole transport agents—DEH, DENH and DECH. With external fields of the order of 100 kV/cm , photorefractive diffraction efficiencies of the order of 10^{-3} were measured. The addition of sensitizer or charge transport agent or both, limits the density of NLO chromophore, thereby considerably reducing the electro-optic coefficient and may result in light scattering due to phase segregation. Ideally the NLO chromophores, sensitizers and charge transport agents should all be incorporated into a polymeric network architecture. This has recently been achieved in our laboratory [8,9] and by Tamura *et al.* [10].

In addition to photoconductivity, photovoltage generation was observed in the poled guest-host NLO polymer. This poled polymer also exhibits a polarization dependent photovoltage when illuminated by light in the absorption region of the NLO chromophore. The physical origin of this effect is a change in the polarization of the medium due to absorption. Similar effects have been reported by Blinov *et al.* [11] in oriented Langmuir-Blodgett films of donor-acceptor molecules.

MATERIALS

For the photoconductivity measurements, three photocrosslinkable polymeric systems have been employed: a guest-host polymer—PVCN (polyvinylcinnamate) / CNNB-R (3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenylazo]nitrobenzene), and two epoxy-based polymeric systems—DGENC—NAC (diglycidyl ether of nitrocathechol/nitroaniline prepolymer functionalized with cinnamoyl groups) and DGEBA—DOAC (diglycidyl ether of bisphenol A / 4[4'-nitrophenylazo] phenylamine [Disperse Orange 3] prepolymer functionalized with cinnamoyl groups). It was reported that these polymer systems when poled exhibit large

second-order optical nonlinearities and can be photocrosslinked, leading to stable second-order NLO materials at room temperature [12–14]. The chemical structures of these polymeric systems were reported elsewhere [12–14]. The polymer films were spin-coated from different polymer solutions on an ITO (indium-tin-oxide) coated glass slide where the transparent ITO layer served as one electrode. These spin-coated films were placed in a vacuum oven at an elevated temperature to remove the residual solvent. A gold layer of 500 \AA thickness was thermally deposited onto the polymer film and this formed the second electrode. This gold layer and the ITO layer sandwich the polymer film. These films were clear and smooth except for few isolated spots when viewed under an optical microscope. The refractive indices of the polymer films were measured using an ellipsometer. The optical absorption spectra for the polymer films were measured with a UV-visible-NIR spectrophotometer and are shown in Fig. 1. The absorption peaks, at 518 nm for PVCN/CNNB-R, at about 373 nm for DGENC-NAC, and at 461 nm for DGEBA-DOAC are

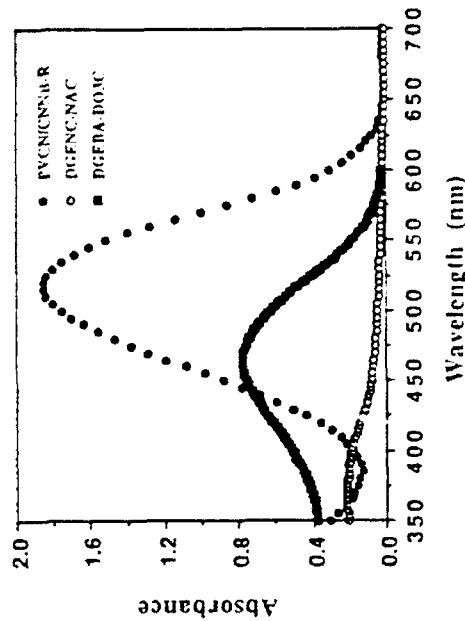


Fig. 1. Optical absorption spectra of the three polymers.

due to the NLO chromophores in each polymer system. For the photoconductivity study, no additional sensitizer and hole transport agents were incorporated into these systems. Additionally, the poled guest-host polymer (PVCN/CNNB-R) was also used in the photovoltage generation study, with either the "sandwich" geometry or the planar gap configuration where the

polymer film was cast across the gap between the two planar electrodes. For the photovoltage measurement, the polymer film was poled at a temperature 5 °C below the glass transition temperature of the material and cooled down to room temperature with the poling field remaining on. The electrodes were then shorted together for few hours before the measurement.

PHOTOCONDUCTIVITY MEASUREMENT

A cw Ar⁺ laser was used in the photoconductivity study. The laser beam illuminates the biased polymer film through an ITO coated glass slide. The photocurrent generated by the incoming photons results in a voltage drop across a 1 MΩ load resistor. This voltage was then measured with a lock-in amplifier in conjunction with a mechanical light chopper. An adjustable neutral density filter was employed to vary the laser intensity incident on the sample. Photoconductivity measurements on these polymer films were performed at various laser intensities, bias voltages and different laser wavelengths.

An approximately linear relationship between the measured photocurrent and the incident laser power, and the bias voltage (V) were observed and are shown in Figs. 2 and 3. The photoconductivity σ_{pc} and the photosensitivity σ_{pc}/I (where I is the laser intensity) were evaluated and are summarized in Table I. The measured photosensitivity compares favorably with the largest value reported in the hole-transport agent doped polymer [5].

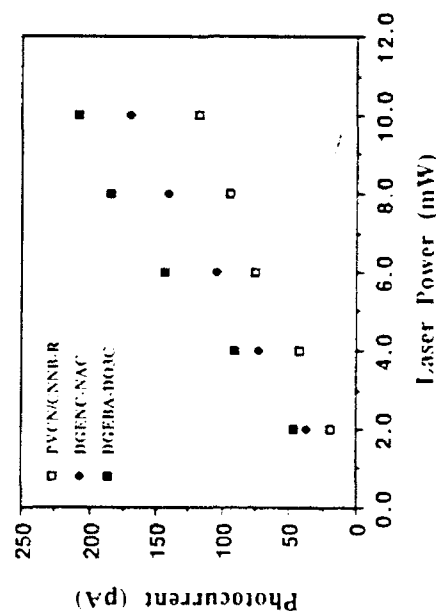


Fig. 2. Effect of laser intensity on photocurrent measured with $V = 10$ V and $\lambda = 514$ nm for PVCN/CNNB-R and DGENC-NAC; and $\lambda = 488$ nm for DGEBA-DO3C.

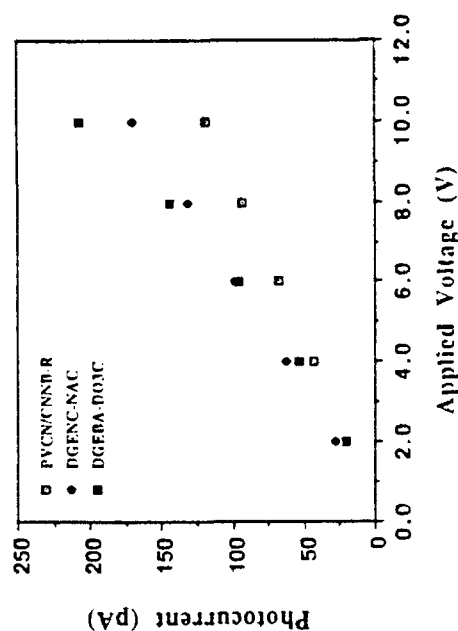


Fig. 3. Effect of bias voltage on photocurrent measured with $I = 0.32$ W/cm² and $\lambda = 514$ nm for PVCN/CNNB-R and DGENC-NAC; and $\lambda = 488$ nm for DGEBA-DO3C.

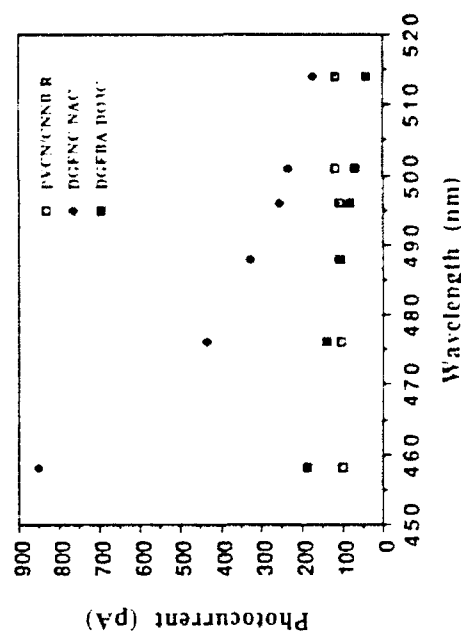


Fig. 4. Spectral dependence of photocurrent measured for the three NLO polymers.

Table I. Optical Properties of the NLO Polymers

	PVCN/CNNB-R	DGENC-NAC	DGEBA-DO3C
Absorp. Peak	518 nm	373 nm	461 nm
Index at 633 nm	1.677	1.680	1.693
d_{33} at 1.064 μm	~ 21.5 pm/V	7.0 pm/V	31.0 pm/V
r_{33} at 633 nm	~ 9.0 pm/V	4.8 pm/V	17.0 pm/V
$\sigma_{pc} \times 10^{-14}$	4.7	19	12
$(\Omega^{-1}\text{cm}^{-1})$	(at 514 nm)	(at 458 nm)	(at 458 nm)
$\sigma_{pc}/I \times 10^{-13}$	1.5	5.9	3.8
$(\Omega^{-1}\text{cm}^{-1}/[\text{W}/\text{cm}^2])$ [at 514 nm]		(at 458 nm)	(at 458 nm)
$Q = n^3 r/\epsilon$	~ 10.6 pm/V	5.7 pm/V	20 pm/V

At fixed laser intensity and bias voltage, the dependence of the photocurrent as a function of laser wavelength (λ) were studied for these polymer films and are shown in Fig. 4. The spectral dependence of the photocurrent shows a behavior similar to the measured optical absorption spectra in the polymer films. This suggests that optical excitation of the NLO chromophores is the origin of photocarrier generation. The donor groups in the NLO chromophores are expected to form stable holes and are conjectured to participate in the charge transport process as well. The photorefractive figure of merit $[5] Q = n^3 r/\epsilon$ for these polymers have been calculated and are summarized in Table I, where the electro-optic coefficients (r) were measured by the method reported earlier [13]. The dielectric constants ϵ of these polymers are in the range of 4-5. For PVCN/CNNB-R (which shows the largest absorption at the Ar^+ laser lines), the photocurrent was found to be insensitive to temperature in the range of 20 to 50 $^\circ\text{C}$ for $T < T_g$, where $T_g = 80$ $^\circ\text{C}$ for this material.

PHOTOVOLTAGE GENERATION

For the study of the photovoltage generation in the poled polymer film, the 514 nm Ar^+ laser line was used as the excitation source. The laser beam illuminates the poled polymer film through an ITO coated glass slide for the "sandwich" configuration or directly onto the gap for the planar gap geometry. The absorption of the incoming photons gives rise to a photovoltage, which was measured with a lock-in amplifier. The polarization dependent

photovoltage measurement was achieved by using a half-wave plate at the wavelength of 514 nm.

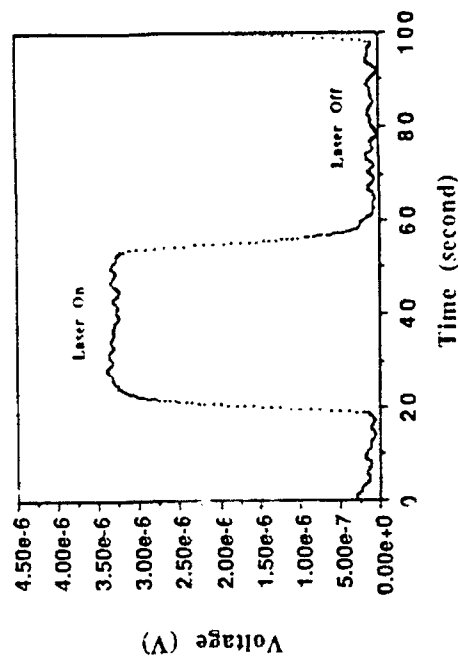


Fig. 5. Photovoltage measured for the sample with the planar gap geometry at $\lambda = 514$ nm with 100 mW laser power.

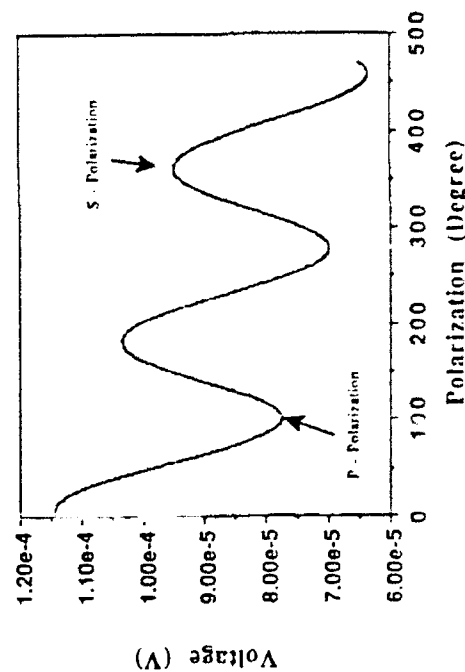


Fig. 6. Polarization dependent photovoltage measured at 514 nm with 10 mW laser power and at 60° incident angle for the sample with "sandwich" geometry.

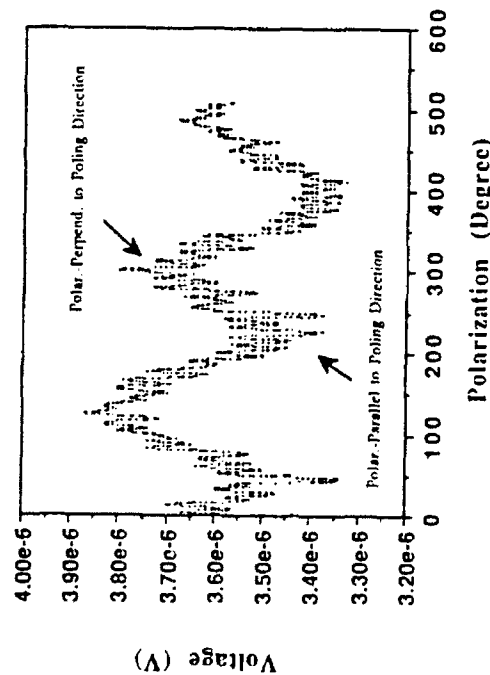


Fig. 7. Polarization dependent photovoltage measured at 514 nm with 100 mW laser power for the sample with the planar gap geometry.

The measured voltage across a load resistor ($R = 100 \text{ M}\Omega$) for the poled guest-host polymer—PVCN/CNNB-R are shown in Figs. 5–7. For the polarization dependent photovoltage measurement, samples with either the "sandwich" geometry or the planar gap geometry were used. For the "sandwich" geometry, the normal to the sample was oriented at an angle of 60° with respect to the laser beam.

CONCLUSIONS

Photoconductivity measurements on three photocrosslinkable second-order NLO polymers as a function of laser intensity, wavelength and applied field were carried out. Photoconductivity and photosensitivity derived from the measured photocurrent in these polymers compare favorably with those polymers using charge transporting agents. In addition to the photoconductivity, photovoltage generation was observed in the poled guest-host polymer (PVCN/CNNB-R). This poled polymer also exhibits a polarization dependent photovoltage when illuminated by light in the absorption region of the NLO chromophore.

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